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Transverse interference peaks in chirp FT-EPR correlated three-pulse ESEEM spectra

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ABSTRACT

Fourier transform (FT) electron paramagnetic resonance (EPR) correlation spectroscopy usually requires broader excitation bandwidth than can be achieved by monochromatic rectangular pulses. Replacement of such pulses by frequency-swept pulses affords the correlation spectra, which, however, may not look the same as those that would be obtained with sufficiently broad-banded monochromatic rectangular pulses. This was recently observed for correlating nuclear frequencies to FT-EPR spectra by a three-pulse electron spin echo envelope modulation experiment. Here we analyze the origin of the additional cross peaks, whose position depends on the direction of the frequency sweep. We find that such peaks arise if coherence or polarization is transferred to an electron spin transition already before this transition is actually passed during the frequency sweep. This happens by excitation of a chain of transitions that connect levels of the source transition, where coherence resides before mixing, and the target transition, where it resides after mixing. The correlation spectra can be simplified by combining data from frequency up and down sweeps.

1. Introduction

When performed on paramagnetic centers, spin echo correlation spectroscopy (SECSY) [1] experiments yield two-dimensional spectra that correlate nuclear frequencies to the Fourier-transform (FT) electron paramagnetic resonance (EPR) spectrum [2]. The nuclear frequencies, which are detected in the indirect dimension, stem from electron spin echo envelope modulation (ESEEM) of the primary or stimulated echo [3]. Recently, it was demonstrated that, by the use of chirp pulses for excitation, such FT-EPR correlated ESEEM spectra can cover an ultra-wide band of up to about 800 MHz in the EPR dimension and detect nuclear frequencies of up to about 200 MHz [4], a range that is not nearly accessible with excitation by monochromatic rectangular pulses. Whereas correlation spectra obtained with the two-pulse SECSY sequence had the same appearance with chirp and monochromatic rectangular excitation pulses, the better resolved correlation spectra obtained with the stimulated SECSY sequence exhibited an unexpected asymmetry. Such an asymmetry was also observed in three-dimensional FT-EPR correlated hyperfine sublevel correlation spectroscopy (HYSCORE) [5] spectra of Cu(II) centers in rutile and of Cu(II) picolinate doped into Zn(II) picolinate [4]. Here we set out to explain how such asymmetry arises and how the position of the originally unexpected peaks depends on spin system parameters and on the sweep direction of the chirp pulses. Such understanding is required for analysis of the spectra and sheds some light on the general phenomenon of transverse interference effects that arise when several connected transitions are passed consecutively during a frequency sweep [6,7].

The paper is organized as follows. In Section 2 we describe the sample of γ-irradiated malonic acid, the experiments and the simulation procedure that we performed in order to clarify the origin of the asymmetry. In Section 3.1 we discuss what conclusions on the origin of the asymmetry can be drawn from experimental spectra obtained with rectangular monochromatic pulses, chirp pulses with upward frequency sweep, and chirp pulses with downward frequency sweep. The relation between coherence transfer pathways and correlation peak positions is explained in Section 3.2. We find that the asymmetry in the correlation spectra depends exclusively on transverse interference during the last chirp pulse. All coherence transfer pathways during this pulse are analyzed in Section 3.3 for the case of a downward chirp applied to a negative hyperfine coupling with a magnitude that exceeds twice the magnitude of the nuclear Zeeman frequency. This case applies to the radical observed in γ-irradiated malonic acid. In the same section we also discuss how the situation changes if the transitions are

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passed in different sequence in an upward chirp. The sequence of passage of the transitions also depends on the signs of the hyperfine coupling as well as the nuclear Zeeman frequency and differs between the strong and weak-coupling cases. The consequences of these differences for the correlation peak pattern are explained in Section 3.4. We conclude by a general assessment of transverse interference effects in correlation spectroscopy based on frequency-swept pulses (Section 3.5).

2. Materials and methods

2.1. Sample

Experiments were performed on a γ-irradiated single crystal of malonic acid in an orientation where the forbidden electron-nuclear transitions are separated from the allowed electron spin transitions in the EPR spectrum.

2.2. Pulse sequence

The SECSY sequence ($\pi/2 - T - \pi - T -$ echo) measures nuclear frequencies through the difference between electron spin transitions. Besides the desired nuclear frequencies ω_α, ω_β, this two-pulse ESEEM also adds combination frequencies to the spectrum, which complicate interpretation. This is avoided by the stimulated SECSY or three-pulse ESEEM sequence ($\pi/2 - \tau - \pi/2 - T - \pi/2 - \tau -$ echo), which exhibits an echo envelope modulation when the delay T between the second and third pulse is varied. The coherence order of the electron spin is zero during T and thus the modulation arises from nuclear coherence, which has been created during the second pulse (also see top panel in Fig. 5) [8]. This avoids combination frequencies, but the different underlying spin dynamics in combination with frequency swept pulses can lead to interference peaks. These interference peaks are only visible in FT-EPR/ESEEM correlation spectra, where a discrimination of the sign in the ESEEM frequency is possible.

2.3. Experiments

All experiments were performed on a home-built high-power EPR spectrometer with arbitrary waveform excitation capability at X-band frequencies around 9.3 GHz [7,9]. Pulse sequences were generated by an arbitrary waveform generator with built-in sequencer (Agilent/Keysight M8190A with up to 12 GSa/s sampling rate) and up-converted to X band by an 8 GHz local oscillator. The same local oscillator was used to downconvert signals to frequencies around 1.3 GHz, with subsequent acquisition with a 2 GSa/s digitizer (SP Devices ADQ412). The pulses, which were amplified by a 1 kW traveling wavetube amplifier (Applied Systems Engineering TWT 117X), were fed to a fully overcoupled Bruker MS3 split-ring resonator with a loaded quality factor $Q_L = 40$ [10]. The spectrometer was controlled by home-written MATLAB scripts. Such scripts were also used for data analysis. All spectra were recorded at room temperature. For the measurements with the monochromatic rectangular pulses we used pulse lengths of 3.5 ns. If all three pulses are swept in the same direction, proper refocusing of the echo and offset-independent evolution during time T is achieved for a pulse length ratio of 2:1:1 [7]. Therefore we used linear chirps with pulse lengths of 200 ns, a rise time of 10 ns and a sweep width of $\Delta f = 200$ MHz in up or down direction. For the monochromatic rectangular pulses the first delay τ was set to 400 ns, for the up-sweep to 277 ns and for the down-sweep to 278 ns. The delay T was incremented from 1.3 μs to 4.3 μs in steps of 6 ns.

2.4. Computations

Numerical simulations were performed with the MATLAB package SPIDYAN 2.0 [11] and analytical computations with the Mathematica package SpinDynamica (see Acknowledgment). For the simulations with SPIDYAN a Hamiltonian of the form $\hat{\mathcal{H}} = \Omega_S \hat{S}_z + \omega_I \hat{I}_z + A\hat{S}_z\hat{I}_z + B\hat{S}_z\hat{I}_x$ was assumed, where the resonance frequency of the electron in the rotating frame Ω_S was Gaussian distributed ($\mu = 1.4$ GHz, $\sigma = 0.8$ MHz). 201 spin packets were taken from a range of $\mu \pm 3\sigma$. The line width in the EPR dimension is controlled through σ and was chosen such that allowed and forbidden transitions are well separated. The resonance frequency $\omega_I/2\pi$ of the nucleus was -14 MHz and for the hyperfine coupling we used $A/2\pi = -45$ MHz and $B/2\pi = +8$ MHz. Simulated monochromatic rectangular pulses had a length of 3.5 ns and chirps 200/100/100 ns, with a rise time of 10 ns and a sweep width of 200 MHz in up or down direction. The first delay τ was set to 400 ns for the rectangular pulses and 278 ns for the chirp pulses. The delay T was incremented from 1.3 μs to 4.3 μs in steps of 6 ns. Any relaxation effects have been neglected during simulations.

In our numerical simulations with density operator formalism, we were interested in signals obtained through the detection operator $\hat{S}^+$. Since $\hat{S}^+$ does not have a Hermitian matrix representation, its pseudo-expectation value must be computed as $\mathrm{Tr}\{\hat{S}^-\sigma\}$ with $\hat{S}^-$ being the lowering operator and σ the density matrix. In contrast to that, we assign peak positions using product operator expressions in Section 3.2, where the term $\hat{S}^+$ corresponds to a change of coherence order $p_S = +1$.

3. Results and discussion

3.1. Appearance of the experimental spectra

Although the asymmetries in chirp FT-EPR correlated three-pulse ESEEM were first noticed on copper(II) centers with nuclear spin $I = 3/2$, we study their origin on the simpler system of an electron spin $S = 1/2$ hyperfine coupled to a nuclear spin $I = 1/2$. Such a system is realized, to a very good approximation, by the radical generated by γ irradiation in solid malonic acid, where the single α proton has a much larger hyperfine coupling than the two protons of the carboxylate groups and the protons in neighboring malonic acid molecules. The proton nuclear Zeeman interaction is negative ($\omega_I/2\pi \approx -14.5$ MHz), as are all principal values of the hyperfine tensor $(A_{xx}, A_{yy}, A_{zz})/2\pi \approx (-60, -93, -28)$ MHz [12]. In almost all orientations the energy level scheme is the one for the strong-coupling case with $A < 0$ shown in the bottom right panel of Fig. 1.

We chose orientations where the splitting between the two allowed transitions in the EPR spectrum slightly exceeds 40 MHz, which is similar to the case considered in the early work on SECSY spectroscopy of this radical [2]. In this situation, the nuclear modulation depth is much larger for the α proton than for the carboxylate protons and correlation of nuclear frequencies to both allowed and forbidden transitions in the EPR spectrum can be observed. The forbidden transitions at frequencies ω_{14} (formally the double-quantum transition) and ω_{23} (formally the zero-quantum transition), which are split by approximately $2\omega_I$, are then observed inside the allowed transitions at frequencies ω_{13} and ω_{24}, the situation corresponding to the bottom right panel in Fig. 2. The absolute values of the nuclear frequencies observed in the three-pulse ESEEM dimension are $\omega_\alpha = |\omega_{12}| = \sqrt{(\omega_I + A/2)^2 + B^2/4}$ and $\omega_\beta = |\omega_{34}| = \sqrt{(\omega_I - A/2)^2 + B^2/4}$, where A is the secular and B is the pseudo-secular contribution of the hyperfine coupling [8].